TEMPORAL BEHAVIOR OF MODULATED REFLECTANCE SIGNAL IN SILICON

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INTRODUCTION

In another paper in these proceedings, Opsal [1] discusses the origin of the modulated reflectance signal observed in silicon under the experimental conditions employed in the Therma-Probe system [2]. These experimental conditions are described in the paper by Smith, Hahn and Arst in these proceedings [3]. Table I lists the major differences between our type of modulated optical reflectance experiments and the more conventional photoreflectance experiments [4-10].

TABLE I: Comparison between our modulated reflectance experiments and conventional photoreflectance experiments.

CONVENTIONAL PHOTOREFLECTANCE	MODULATED OPTICAL REFLECTANCE
PUMP BEAM < 1 W/cm^2 PROBE BEAM < 1 mW/cm^2	PUMP BEAM > 10^4 W/cm^2 PROBE BEAM > 10^3 W/cm^2
BEAM SPOTS ~ mm	BEAM SPOTS ~ 1 μm
PUMP MODULATION < 1 kHz	PUMP MODULATION ~ MHz
PROBE λ SCANNED SPECTROSCOPY-CRITICAL POINTS → BAND STRUCTURE	PROBE λ FIXED TRANSPORT PROPERTIES OF THERMAL & PLASMA WAVES
NON-SEMICONDUCTORS; SIGNAL FROM THERMOREFLECTANCE	NON-SEMICONDUCTORS; SIGNAL FROM THERMOREFLECTANCE
SIGNAL IN SEMICONDUCTORS; FROM ELECTROREFLECTANCE	SIGNAL IN SEMICONDUCTORS; FROM THERMOREFLECTANCE AND DRUDE EFFECTS
NONLINEAR IN PUMP INTENSITY NO TEMPORAL BEHAVIOR	LINEAR IN PUMP INTENSITY TEMPORAL BEHAVIOR -LASER "ANNEALING" EFFECT-

Of particular interest are the facts that: 1) in our modulated reflectance experiments the main source of signal appears to come from thermoreflectance and Drude effects from the electron-hole plasma [1,11] rather than the electroreflectance effects [12] that tend to dominate the photoreflectance signal; and 2) that the modulated optical reflectance signal appears to exhibit a temporal or laser "annealing" behavior under continuous laser irradiation whereas no such temporal behavior has been observed in photoreflectance.

As described in the paper by Opsal [1], the Drude portion of the modulated reflectance signal in a semiconductor like silicon may be written as the sum of three terms:

$$\Delta R/R = [\Delta R/R]_0 |1 - \alpha[(1 - i\omega\tau_1)^{-1} + \beta(1 - i\omega\tau_2)^{-1}]| \qquad (1)$$

where the first term is the Drude term arising from the <u>free</u> photogenerated carriers; the second term is the Drude term from those photogenerated carriers that are temporarily pinned or trapped at the surface by intrinsic (i.e., dangling-bond) surface states: and the third term is the Drude term from the photogenerated carriers that are temporarily pinned or trapped at the surface by extrinsic (i.e., defect or impurity related) surface states. Expressions and definitions for the various terms and symbols in Eq.(1) are given in [1].

Continuous laser irradiation is assumed to have no effect on the intrinsic dangling-bond surface states as long as the laser intensity is non-damaging. However, it is possible that even non-damaging laser irradiation may electronically modify the extrinsic or defect-related surface states through the presence of a high density of photogenerated carriers. Thus we may hypothesize that while α in Eq.(1) may be time-independent, β may be time-dependent. Our results, as discussed below, indicate that $\beta \to 0$ as $t \to \infty$ under continuous intense laser irradiation.

EXPERIMENTAL RESULTS

Our experiments on incoming bare silicon wafers show that typical modulated reflectance signals, $\Delta R/R$, at 1 MHz lie in the range of $0.3\text{-}2\times10^{-3}$. Our data indicate that the higher signal levels are indicative of the small amount of residual damage present in the surface regions of the wafers that result from the chemipolishing and scrubbing processes used in the final stages of the manufacture of the wafers [3]. As described by Opsal [1], theoretical calculations predict that the modulated reflectance signal should generally increase with the extent of damage, in the form of surface states or of lattice disorder in the near surface region of the silicon wafer. These theoretical predictions are in agreement with experimental results on both incoming wafers and on ion-implanted wafers [3,13]. In Fig. 1 we see that the lowest signal is for an incoming wafer that has been thermally annealed and has several hundred Angstroms of thermal oxide grown on it. This wafer would be expected to have the least amount of damage, both from the thermal annealing and from the consumption of any damaged silicon region by the growth of the oxide film. Our experiments on ion-implanted wafers [13,14] show that the modulated reflectance signal increases monotonically with the dose of implanted ions into the wafer. Furthermore when an implanted wafer is thoroughly annealed the $\Delta R/R$ signal decreases dramatically. All of these results indicate that the modulated reflectance signal tends to increase with the amount of damage in the near surface region of the wafer.

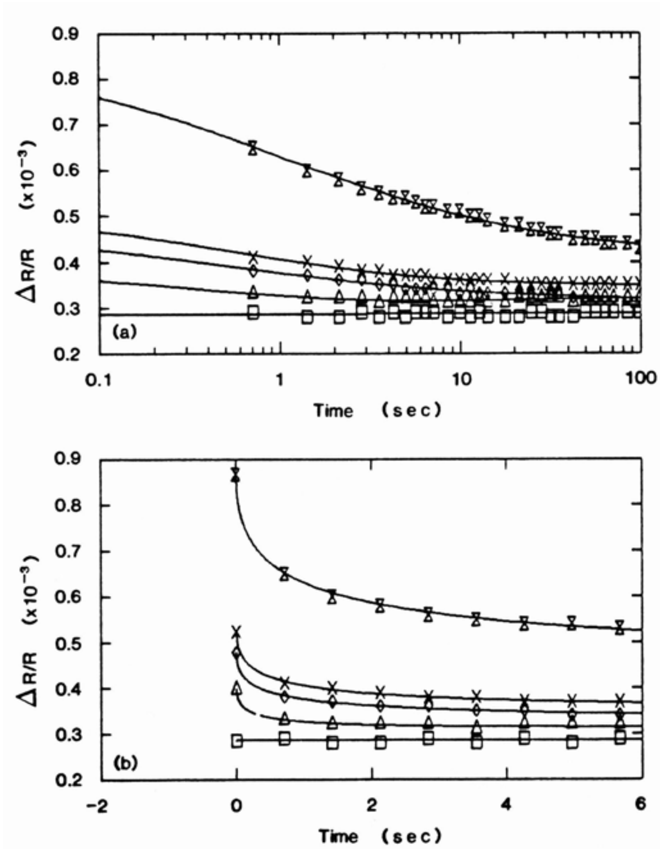

Fig. 1 Modulated reflectance as a function of time on a number of different silicon samples: □ - Si with 300 Å thermal-oxide film, Δ - p-Si 5 Ω-cm (#1), ◇ - p-Si 50 Ω-cm, X - p-Si 5 Ω-cm (#2), ⧗ - p-Si 5 Ω-cm (#3, 3 x polishing pressure). The lower plot in this figure and in all subsequent plots of temporal data shows the behavior near t = 0.

Returning to Fig. 1, we see that except for the wafer with the thermal-oxide film, all other incoming "bare" wafers tend to exhibit a temporal dependence of the signal, that is, the magnitude (and often the phase) of the ΔR/R signal changes if the pump and probe laser beams are allowed to continually illuminate the same spot on the silicon wafer. Of considerable importance is the fact that the time-dependent curves can be fit with high accuracy to an expression of the form,

$$f(t) = A\{1 + B\exp(Ct)\mathrm{erfc}(\sqrt{Ct})\} \quad , \qquad (2)$$

thus indicating that this laser-induced temporal effect is a result of a diffusion process. This particular solution of the the diffusion equation [15] corresponds to having a source term which decays exponentially in time as exp(-Ct) and should therefore approximate the removal of the defect surface states from the illuminated region that we believe is occuring in our measurements. We will henceforth refer to this laser-induced temporal effect on the $\Delta R/R$ signal as a laser annealing effect. Using Eq.(2) we are then able to predict the $t = \infty$ value of the $\Delta R/R$ signal and this value is indicated in Table II for the various wafers. We note that the $t = \infty$ signal as well as the $t = 0$ signal are lowest for the silicon wafer with the least amount of damage, that is, the wafer with the 300 Å of thermal oxide film. On the other hand, both the $t = 0$ and $t = \infty$ signal levels for the other wafers vary considerably and these variations appear to be related to the amount of near-surface damage present and to the amount of intrinsic disorder from the as-grown dopant concentrations. Thus a heavily doped (not shown) p-Si wafer with 0.01 Ω-cm resistivity exhibits the highest $t = \infty$ signal. We attribute the increased $t = \infty$ signal for the heavily doped 0.01 Ω-cm wafer to the effects of the high doping concentration on the the electron-hole diffusivity D (with the understanding of course that the recombination lifetime τ and the surface recombination velocity S may also be affected).

TABLE II: Actual $t = 0$ and predicted $t = \infty$ values for the modulated reflectances shown in Fig. 1.

Sample	$\Delta R/R$ at $t = 0$ ($\times10^{-3}$)	$\Delta R/R$ at $t = \infty$ ($\times10^{-3}$)
Si with 300 Å thermal-oxide film	0.285	0.286
p-Si 5 Ω-cm (#1)	0.397	0.326
p-Si 50 Ω-cm	0.477	0.312
p-Si 5 Ω-cm (#2)	0.523	0.345
p-Si 5 Ω-cm (#3) (3 x polishing pressure)	0.867	0.404

However if we compare the 5 Ω-cm (#1) wafer with the 50 Ω-cm wafer, we see that their $t = \infty$ signals are essentially identical, indicating that a change in doping concentration by a factor of 10 does not noticeably change the intrinsic $\Delta R/R$ signal when the doping concentration is low. Nevertheless these two curves have different $t = 0$ values, possibly indicating different amounts of near surface damage.

In fact if we compare three 5 Ω-cm wafers (#1,2 and 3) that have received different polishing treatments with wafer #1 receiving that polishing treatment that is considered to produce minimal damage while wafer #3 received the most damage, it is clear that the $t = 0$ signal is especially sensitive to the presence of this damage while the $t = \infty$ signal is less so. We are able to account for this observation by assuming that chemipolishing damage results in both some lattice disorder and, more significantly, in the presence of additional extrinsic, i.e., impurity or defect surface states. Since our laser beams are generating temperatures of only ~ 10°C, we would not expect any laser annealing effect on the lattice disorder damage. However, as we postulate [1], it may be possible that extrinsic non-dangling bond surface states may be altered, by charge neutralization, bond reconfiguration or promotion into another state such as a bulk defect state, by the presence of the photogenerated electron-hole plasma. In particular the energy for the alteration of the extrinsic surface states may come from a local electron-hole recombination event. This may be analogous to the photogeneration of recombination defects in amorphous silicon.[16-18] At any rate we would thus expect that while the t = 0 signal is indicative of the presence of both extrinsic surface states and lattice disorder, the t = ∞ signal would be mostly due to the amount of lattice disorder present, with most of the extrinsic surface states "annealed" out by the laser beams. This explanation is consistent with the observation that silicon wafers with a thermally grown oxide film exhibit no laser annealing effect. It is well known that a good Si/SiO_2 interface will have only dangling bond interface states and that these would not be altered by the presence of an electron-hole plasma or by local electron-hole recombination events. On the other hand extrinsic, i.e. impurity or defect-related, surface states may be altered by the electron-hole plasma and by electron-hole recombination events.

Similar results are obtained with epitaxial silicon wafers. Although epitaxial films are usually of higher crystalline quality than as-grown bulk Si, these films can exhibit high concentrations of extrinsic surface defect states from the hydrogen that is incorporated into the surface layers during the epitaxial growth reaction.

Thermal Effects

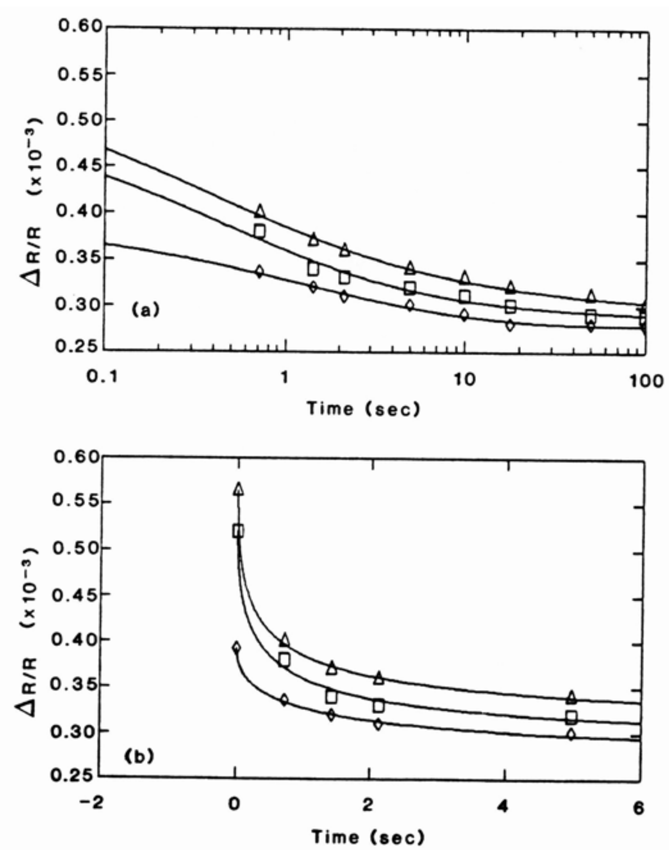

Fig. 2 Modulated reflectance as a function of time showing effects of heat treatment on a 0.21 Ω-cm epitaxial Si sample: ◇ - after 30 minutes at 200°C, □ - 72 hours after thermal treatment, Δ - before heat treatment.

In Fig. 2 we show the temporal behavior of the ΔR/R signal for a 0.21 Ω-cm epitaxial Si Film before and after a thermal anneal at a fairly low temperature of 200°C. We note that while such low temperatures appear to have little noticeable effect on the t = ∞ signal, this is not true for the t = 0 signal. In fact after only 30 minutes at 200°C, the t = 0 signal decreases substantially. However, of even greater interest is the fact that if the wafer is then reexamined after another 72 hours at room temperature in air, most of the original t = 0 signal returns. Other experiments on various bulk and epitaxial wafers have confirmed these findings. Thus moderately low temperature thermal annealing in air tends to have the same effect on the extrinsic surface states as does the laser annealing. This indicates that the activation energy for neutralizing or transforming these extrinsic surface states is indeed quite small, in keeping with the concept that the laser annealing effect is a result of an electron-hole recombination phenomenon. The fact that the thermal annealing of these states is reversible is also in keeping with the diffusion aspects of the laser annealing effect.

Effect of Ion Implantation

In Fig. 3 we show how the t = 0 and t = ∞ ΔR/R signals vary with boron and arsenic implant into Si wafers. Of considerable importance is the observation that the t = ∞ signal increases rapidly with increasing implant dose, thus indicating that the major portion of the ΔR/R signal arises from lattice disorder.

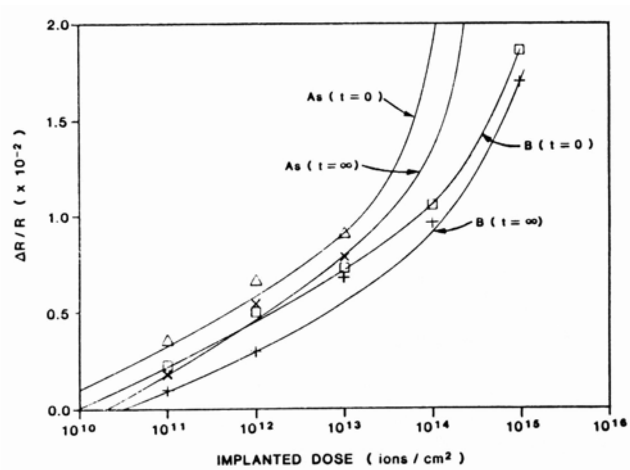

Fig. 3 Modulated reflectance signal as a function of implanted dose at t = 0, and t = ∞.

Although some of the implant-generated damage is due to extrinsic surface states, the data in Fig. 3 indicate that the contribution to the total signal from these implant-generated extrinsic surface states does not increase as rapidly as does the contribution from the lattice disorder itself.

As we noted before, a Si wafer with a thermal oxide film exhibits no laser annealing behavior. However, this is not true of such a wafer which is then implanted. The implantation process disrupts the Si/SiO_2 interface and allows the creation of extrinsic interface states associated with either localized structural defects or with implanted dopant ions and other impurities at the Si/SiO_2 interface. Thus, similar t = 0 and

$t = \infty$ data are obtained for implants on oxidized wafers as on bare wafers.

However, implanted oxide coated wafers exhibit quite different behavior from implanted bare wafers after a high temperature anneal. While bare wafers will initially exhibit no temporal dependence or laser annealing behavior immediately after the high temperature anneal, this behavior will manifest itself a few days later. This result is similar to that observed for unimplanted epitaxial films or polished bulk wafers. However, wafers that have been implanted through a screen or gate oxide permanently lose all evidence of any laser annealing behavior after a high temperature thermal anneal. This indicates that once the high temperature post-implant thermal anneal heals the Si/SiO_2 interface, the extrinsic interface states are either removed or acquire too high an activation energy to be altered by the laser beams. This is consistent with our prior observations of no temporal dependence in Si wafers having a good thermal oxide film.

Duration of Laser Annealing Effect

We have investigated the duration of the laser annealing effect by first irradiating a fairly large area on a Si wafer until its modulated reflectance signal reaches its steady state condition (i.e. the $t = \infty$ level). We then perform some quick checks on the signal from this region as a function of time. These quick checks are performed in a manner so as to minimize as much as possible any additional laser annealing effect from the checks themselves. Our results indicate that the signal slowly comes back to its initial $t = 0$ level in a diffusive fashion. However, whereas the laser annealing effect occurs within minutes, the return of the signal to its initial $t = 0$ level usually takes several days.

This is similar to the results obtained for thermal annealing, thus indicating that the annealed state is in both cases a metastable state that will in time revert back to its original extrinsic surface state at room temperature.

Spatial Extent of Annealing Effect

Of considerable interest is the spatial extent of this laser annealing effect. This experiment is performed by illuminating a micron sized spot on the silicon wafer for 60 seconds until a reasonably annealed state is achieved, then rapidly moving a set distance from this location and recording the $t = 0$ signal at the new location. By repeating this procedure many times we are able to map out the spatial extent of the annealing effect after a 60 second exposure at a given site. The data obtained indicate that in Si wafers with high levels of structural damage such as heavily implanted wafers, the annealing effect appears to be confined to the irradiated site. However for wafers that have little or no structural damage such as starting Si wafers or epitaxial films, the laser annealing effect appears to extend 50-100 μm beyond the initial illuminated point after 60 seconds. This is most surprising since three-dimensional calculations readily show that neither the DC nor the AC thermal waves and electron-hole plasma waves extend much beyond 5-10 μm from the illuminated spot.

These data indicate that the laser annealable surface states either diffuse away from the illuminated area under their own concentration gradient, or that a neutralyzing factor diffuses out from the illuminated area. This neutralizing factor may be a trapped charge from the photogenerated carriers that can hop or diffuse a considerable distance away from the irradiated area provided the Si crystal has little or no structural damage.

SUMMARY

We have presented laser-induced modulated reflectance data on crystalline silicon, epitaxial silicon, and ion-implanted, but unannealed, silicon which in general is dependent on the time of exposure to the pump and probe beam illumination. This effect, which is reversible, appears to be a new phenomenon, certainly for crystalline and epitaxial silicon, and related to the presence and temporal evolution of electronic surface states. To support our conjecture that electronic surface states are involved, we have shown data on samples which have undergone different surface treatments as well as a number that have been ion implanted. This temporal behavior, which we have termed a laser annealing effect, is present to varying degrees in all samples and appears to depend on the amount of surface damage. In addition, the effect completely disappears for samples with a thermally grown oxide as well as on samples that have been implanted through a screen or gate oxide and then subjected to a high temperature anneal. Finally, our data on bare silicon wafers having little surface damage shows that the laser annealing effect can extend well beyond the area of illumination indicating that a surface diffusion process may be taking place.

In conclusion, we want to emphasize that this laser annealing effect is reproducible and appears to be well correlated with surface conditions. Thus we believe that, in addition to its potential for providing more information about electronic surface states in silicon (and perhaps in other semiconductors as well), the temporal behavior of the laser-induced modulated reflectance can be used in practice as a nondestructive method for semiconductor surface characterization.

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